

## 7020 QUALITY ASSURANCE/QUALITY CONTROL\*

### 7020 A. Basic Quality Control Program

#### 1. Introduction

Every laboratory that performs radionuclide analyses for environmental water and wastewater samples should have a written and operating quality assurance (QA) plan. This plan can be a separate document or can, by reference, use parts of existing standard operating procedures (SOPs). The quality-control (QC) portion of the QA plan addresses instrumental, background, accuracy, and precision QC. Also essential is a manual of analytical methods, or at least copies of approved methods, available to the analysts.

#### 2. Performance Criteria

For a successful QC program, select acceptable and attainable performance criteria for precision and accuracy. These criteria

must reflect the capabilities of the laboratory and the purposes for which the data are to be used.

Performance criteria can be drawn up initially from experience with the analytical method or from criteria set by other laboratories using the same procedure. A tabulation of allowable deviations used by the EPA<sup>1</sup> is given in Table 7020:I. The criteria are a function of the particular analysis under study. A laboratory might use these or other published values until enough data can be compiled to set its own criteria from experience.

#### 3. Minimum Quality Control Program

A radiochemistry QC program is composed of a number of integrated functions, including instrumental, background, precision, and accuracy QC.

A useful way of keeping track of instrument and background performance is through control charts. Certain aspects of radio-

\*Approved by Standard Methods Committee, 1996.

chemical instrument and background QC are instrument- or method-specific and are dealt with in the individual methods.

The instrumental control charts<sup>2</sup> are prepared by plotting counts of a reference source on a graph showing time as the abscissa and count rate or total counts as the ordinate. Lines are drawn parallel to the time axis at values (corrected for decay if necessary) for the "true" count rate and for values of  $\pm 2$  and  $\pm 3$  standard deviations. The true count rate is determined by averaging at least 20 counts with acceptable individual statistics.

Interpret quality control chart data objectively. When a point goes outside the limits, determine whether instrument service is necessary or the result is simply a random occurrence by running a series of repeated measurements and applying another statistical test, such as a Chi-square test, to determine whether the variation was nonstatistical.

Trends from control charts may show other information. For example, if regular measurements of the check source show a movement in one direction, one can infer that some system variable is changing. This variation may not always require instrument service; instead the values of the limits or the "true" value may need to be reevaluated.

*a. Instrumental QC:* For alpha and beta counters, count check source daily (or before each use) for a predetermined time. Record count rate and plot it on the control chart for the specific system. Compare this value with the  $\pm 2 \sigma$  (warning) limits and the  $\pm 3 \sigma$  (out-of-control) limits, and repeat the procedure if the  $\pm 2 \sigma$  boundary is exceeded. Take appropriate action if repeated values are above the warning levels.

For instruments that produce spectra, such as gamma or alpha spectrometers, many parameters can be tracked, including efficiency response, i.e., count rate or total counts in a given spectral area; peak channel location of one or more spectral photopeaks; difference in channels between two specified peaks; resolution, i.e., width of peak in channels at specified peak height; and certain

ratios such as "peak to compton." It is not necessary to track all of these routinely; see specific recommendations in Section 7120. If these basic parameters are outside the limits, other parameters may need to be evaluated.

*b. Background QC:* At defined frequencies, such as daily or before each use for proportional or liquid scintillation counters, count background for each system for the standard counting time. Make background measurements with each batch of samples. Spectrometers may require specific treatment because background is determined from the sample spectrum in the analysis of activity. In this specific case, longer background counts at less frequent intervals (for example, weekly) may be needed to produce reasonable counts in specific regions of interest.

Record background counts and plot them on control charts. Obtain background "true value" by averaging at least 20 background counts. Calculate 2 and 3  $\sigma$  counting errors based on the average value and the background counting time. Take appropriate actions in the event of background or standard reference count problems.<sup>2</sup>

Background QC is specific to the type of counting instrument. For instance, gamma spectroscopy background QC represents a specific challenge depending on whether the detector is NaI(Tl) or germanium; see Section 7120.

Analyze reagent blanks often enough to ensure the absence of major interference that would bias the reported results. Ideally, results for a reagent blank will be identical to the background, e.g., for an analysis using a proportional counter, identical to the counts from a blank planchet.

*c. Precision QC:* Evaluate laboratory's internal precision in performing an analytical procedure by analysis of blind duplicate samples, that is, duplicate portions of randomly selected samples submitted as new samples. It is important that the analyst be unaware either that a given sample will be resubmitted or that it is a reanalysis. This may be difficult in a small laboratory. It is

TABLE 7020:I. LABORATORY PRECISION—ONE STANDARD DEVIATION VALUES FOR VARIOUS ANALYSES IN WATER SAMPLES

Analysis	Activity Level pCi/L	One Standard Deviation for Single Determination	Control Limits*
Gamma-emitters	5 to 100	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>100	5% of known value	$\mu \pm 0.087 \mu$
Zinc-65, barium-133, ruthenium-106	5 to 50	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>50	10% of known value	$\mu \pm 0.17 \mu$
Strontium-89, strontium-90	5 to 100	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>100	5% of known value	$\mu \pm 0.087 \mu$
Gross alpha	$\leq 20$	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>20	25% of known value	$\mu \pm 0.43 \mu$
Gross beta	$\leq 50$	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>50 to 100	10 pCi/L	$\mu \pm 17.3$ pCi/L
	>100	15% of known value	$\mu \pm 0.26 \mu$
Tritium	<4000	$170 \times (\text{known})^{0.0933}$	$\mu \pm 294 \times (\mu)^{0.0933}$
	$\geq 4000$	10% of known value	$\mu \pm 0.17 \mu$
Radium-226	$\leq 0.1$	15% of known value	$\mu \pm 0.26 \mu$
Radium-228	$\leq 0.1$	25% of known value	$\mu \pm 0.43 \mu$
Iodine-131	$\leq 55$	6 pCi/L	$\mu \pm 10.4$ pCi/L
	>55	10% of known value	$\mu \pm 0.17 \mu$
Uranium	$\leq 35$	3 pCi/L	$\mu \pm 5.2$ pCi/L
	>35	10% of known value	$\mu \pm 0.17 \mu$

\*Average of three determinations.  $\mu$  = known value.

important also that samples submitted for duplicate analysis have detectable amounts of radioactivity so that statistical treatment of data does not consist of comparing zeros or "less than" values. In some cases, it may be necessary to substitute samples with known additions for routine workload samples.

Preferably analyze 10 percent duplicate samples to verify internal laboratory precision for a specific analysis; this is a general guideline and may be varied to fit the situation. For example, for a laboratory with a heavy workload and a well-established duplicate analysis program, 5 percent duplicate samples or 20 samples per month may be sufficient to determine whether the data meet established criteria. A discussion of the statistical treatment of duplicate analysis data is given elsewhere.<sup>2,3</sup> One criterion for acceptability of duplicate measurements is given in EPA's Drinking Water Certification Manual. The difference between duplicate measurements should be less than two times the standard deviation of the specific analysis as described in Table 7020:I.<sup>4</sup> If the difference between duplicates exceeds two standard deviations, prior measurements are suspect; examine calculations and procedures and reanalyze samples when necessary.

*d. Accuracy QC:* Analytical methods are said to be in control when they produce results that are both precise and unbiased. Evaluate accuracy by preparing or obtaining water samples of known radionuclide content, analyzing them, and comparing the results to the known values. Plot data from these standards or known-addition samples on means or individual results control charts,<sup>2,3</sup> and determine whether or not results from these samples are within the control limits and/or warning limits set on the control charts. Laboratories also can set accuracy limits for samples with known additions based on percent recovery of the known value. Preferably run a known-addition or standard sample with each batch of samples. If the known-addition value is outside the limits, investigate method bias. All sample results are suspect until the known-addition results are back within the prescribed limits.

To be certified to perform drinking water analyses under the Safe Drinking Water Act, a laboratory must participate successfully at least three times each year in those EPA laboratory performance evaluation studies that include each of the analyses for which the laboratory is, or wants to be, certified. Two of these studies must be constituent-specific and one must be a mixed blind performance evaluation sample. Analytical results must be within control limits established by EPA for each analysis for which the laboratory is, or wants to be, certified.<sup>1</sup>

Laboratories are encouraged to participate in intercomparison programs such as those sponsored by USEPA,<sup>1</sup> International Atomic Energy Agency (IAEA),<sup>†</sup> and World Health Organization (WHO).<sup>‡</sup>

*e. Selection of radionuclide standards and sources:* Calibrated radionuclide standard solutions are prepared for storage and shipment by the supplier in flame-sealed glass ampules. Preferably perform all dilutions and storage of radionuclides in glass containers and avoid the use of polyethylene.

Standard sources are radioactive sources having adequate activity and an accurately known radionuclide content and radioactive decay rate or rate of particle or photon emission. Each radionuclide standard should have a calibration certificate containing the following information:

<i>Description:</i>	<i>Purity:</i>
Principal radionuclide	Identification of impurities
Chemical form	Activity
Solvent	Included or not included in principal activity
Carrier and content	
Mass and specific gravity or volume	<i>Assumptions:</i>
<i>Standardization:</i>	Decay scheme
Activity per mass or volume	Half-life
Date and time	Equilibrium ratios
Activity of daughter	<i>Production:</i>
Method of standardization	Production method
<i>Accuracy:</i>	Date of separation
Repeatability error	<i>Usable lifetime</i>
Systematic error	
Overall error	
Confidence levels	

Confirm that radionuclide standard sources are traceable to the National Institute of Standards and Technology (NIST). Use such standard sources, or dilutions thereof, for initial calibration. These sources may be purchased from suppliers listed in annually published buyers' guides. Before purchasing standards from commercial suppliers, inquire as to the traceability of the particular radionuclide of interest. A good discussion of NIST traceability is given elsewhere.<sup>5</sup> Example of radionuclide calibration certificates and NIST traceability certificates have been published.<sup>1</sup> At present, standardized radioisotope solutions can be purchased from the IAEA<sup>†</sup> and NIST.<sup>§</sup> Participants in USEPA's Performance Evaluation Studies Program can obtain standardized radionuclide solutions on request.

Use check sources for determining changes in counting rate, counting efficiency, and/or energy calibration. These sources should be of sufficient radiochemical purity and activity to permit correction for decay, but they need not have an accurately known disintegration rate (i.e., need not be a standard source).

Standard reference materials (SRMs) are radioactive materials having adequate activity and accurately known radionuclide content and radioactive decay rate or rate of particle or photon emission. They may be used as internal laboratory control samples, internal tracers, or matrix and blind known additions. They should have calibrations traceable to NIST or equivalent.

#### 4. References

1. DILBECK, G. & P. HONSA. 1994. Environmental Radioactivity Performance Evaluation Studies Program and Radioactive Standards Distribution Program. ORD EMSL-LV, U.S. Environmental Protection Agency, Las Vegas, Nev.
2. KANIPE, L.G. 1977. Handbook for Analytical Quality Control in Radioanalytical Laboratories. E-EP/77-4.TVA.EPA-600/7-77-038, Section 3, U.S. Environmental Protection Agency, Washington, D.C.
3. ROSENSTEIN, M. & A.S. GOLDIN. 1964. Statistical Techniques for Quality Control of Environmental Radioassay. AQCS Rep. Stat-1, U.S. Dep. Health, Education & Welfare, PHS, DRH, Winchester, Mass.

<sup>†</sup>International Atomic Energy Agency, Analytical Quality Control Services, Seibersdorf, P.O. Box 100, A-1400, Vienna, Austria.

<sup>‡</sup>World Health Organization, Geneva, Switzerland.

<sup>§</sup>U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology, Standard Reference Materials Program, Building 202, Room 204, Gaithersburg, MD 20899.

4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Manual for the Certification of Laboratories Analyzing Drinking Water. EPA/570/9-90/008, OGWDW (WH-550D), Office of Ground Water and Drinking Water, Washington, D.C.

5. NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1985. A Handbook of Radioactivity Measurements Procedures. NCRP Rep. No. 58, National Council on Radiation Protection and Measurements, Bethesda, Md.

## 7020 B. Quality Control for Wastewater Samples

Generally it is not feasible to perform collaborative (interlaboratory) analyses of wastewater samples because of the variable composition of elements and solids from one facility to the next. The methods included herein have been evaluated by use of homogeneous samples and are useful for nonhomogeneous samples after sample preparation (wet or dry oxidation and/or fusion and

solution) resulting in homogeneity. Reference samples used for collaborative testing may be deficient in radioelements exhibiting interferences because of decay during shipment of short-half-life-radionuclides. Generally, however, analytical steps incorporated into the methods eliminate these interferences, even though they may not be necessary for the reference samples.

## 7020 C. Statistics

Section 1030 discusses statistics as applied to analysis of chemical constituents. It is applicable also to radioactivity examinations; however, certain statistical concepts peculiar to radioactivity measurements are discussed below.

### 1. Propagation of Errors

Often it is necessary to calculate the uncertainty of a quantity that is not measured directly, but is derived, by means of a mathematical formula, from directly measured quantities. The uncertainties of the latter are known or can be computed and the uncertainty of the calculated quantity derived from them. Statistically, this is known as propagation of errors. One of the more common applications of propagation of errors is in combining all the sources of error in determining pollutant concentrations in environmental samples such as soil, air, milk, or water. These data include errors from sampling, analysis, and other variables, all of which must be considered in determining the total variability or variance.

The formula for propagation of errors states that when quantities are added or subtracted, the combined error ( $\sigma_T$ ) is equal to the square root of the sum of the squares of the individual errors.

$$\sigma_T = (\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \dots + \sigma_n^2)^{1/2}$$

The propagation of errors law application is possible because variance is an additive property:

$$\sigma_T^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \dots + \sigma_n^2$$

A number of propagation-of-error formulas have possible application to the determination of radionuclide concentrations in water.<sup>1</sup> The most common of these are given in Table 7020:II. The one most widely used in nuclear counting statistics is the first formula, where  $X$  represents the activity (counts) of sample + background, and  $Y$  represents the activity of the background.

TABLE 7020:II. PROPAGATION-OF-ERROR FORMULAS

Function	Error Formula
$Q = X \pm Y$	$\sigma_Q = (\sigma_x^2 + \sigma_y^2)^{1/2}$
$Q = aX + bY$	$\sigma_Q = (a^2\sigma_x^2 + b^2\sigma_y^2)^{1/2}$
$Q = XY$	$\sigma_Q = XY \left( \frac{\sigma_x^2}{X^2} + \frac{\sigma_y^2}{Y^2} \right)^{1/2}$
$Q = \frac{X}{Y}$	$\sigma_A = \frac{X}{Y} \left( \frac{\sigma_x^2}{X^2} + \frac{\sigma_y^2}{Y^2} \right)^{1/2}$

### 2. Standard Deviation and Counting Error

The variability of any measurement is described by the standard deviation, which can be obtained from replicate determinations. There is an inherent variability in radioactivity measurements, due to the random nature of radioactive decay, which is described by the Poisson distribution. This distribution is characterized by the standard deviation of a large number of events,  $N$ , that equals its square root, or:

$$\sigma(N) = N^{1/2}$$

When  $N > 20$ , the Poisson distribution approximates the normal (Gaussian) distribution. This approximation simplifies the computation of confidence intervals and permits reasonably accurate estimates of the mean and variance of the distribution of results without performance of replicate counts.

More often, the variable of concern is the standard deviation in the counting rate (number of counts per unit time):

$$R' = \frac{N}{t}$$

where:

$t$  = duration of counting.

The standard deviation of the counting rate, when the appropriate substitutions are made, is:

$$\sigma(R') = \frac{N^{1/2}}{t} = \frac{(R't)^{1/2}}{t} = \left(\frac{R'}{t}\right)^{1/2}$$

In practice, all counting instruments have a background counting rate,  $B$ , when no sample is present. With a sample, the counting rate increases to  $R_o$ . The net counting rate,  $R$ , due to the sample is:

$$R = R_o - B$$

By propagation-of-error methods, the standard deviation of  $R$ , the net counting rate, is calculated as follows:

$$\sigma(R) = \left(\frac{R_o}{t_1} + \frac{B}{t_2}\right)^{1/2}$$

where:

$R_o$  = gross counting rate,

$B$  = background counting rate, and

$t_1, t_2$  = elapsed counting times at which gross sample and background counting rates were measured, respectively.

Counting duration for a given set of conditions depends on the limit of detection required (see below). Preferably divide the counting time into equal periods to check constancy of observed counting rate. For low-level counting, where net count rate is of the same order of magnitude as the background, use  $t_1 = t_2$ . The error thus calculated includes only uncertainty caused by inherent variability of the radioactive disintegration process and is not the standard deviation of the total analysis. The counting uncertainty is the major portion of the total uncertainty at or near the limit of detection. As concentration levels increase, the percent counting error decreases and systematic errors become the major portion of total error.

Use a confidence level of 95%, or 1.96 standard deviations, as the counting error. Report radioactivity concentration results with the counting error as  $X \pm 1.96\sigma$ , both in pCi/L.

### 3. Limit of Detection

Various conventions have been used to estimate the lower limit of detection (LLD) or the minimum detectable activity (MDA). The procedure recommended here, used at the Environmental Measurements Laboratory,<sup>2</sup> is based on hypothesis testing.<sup>3</sup>

The LLD is defined as the smallest quantity of sample radioactivity that will yield a net count for which there is a predetermined level of confidence that radioactivity will be measured. Two errors may occur: Type I, in which a false conclusion is reached that radioactivity is present, and Type II, with a false conclusion that radioactivity is absent.

The LLD may be approximated as follows:

$$LLD = (K_\alpha + K_\beta)S_o$$

where:

$K_\alpha$  = value for upper percentile of standardized normal variate corresponding to preselected risk of concluding falsely that activity is present ( $\alpha$ ),

$K_\beta$  = corresponding value for predetermined degree of confidence for detecting presence of activity ( $1-\beta$ ), and

$S_o$  = estimated standard error of net sample counting rate.

For sample and background counting rates that are similar (as is expected at or near the LLD) and for  $\alpha$  and  $\beta$  equal to 0.05, the smallest amount of radioactivity that has a 95% probability of being detected is,

$$LLD_{95} = 4.66 S_b$$

where:

$S_b$  = standard deviation of background counting rate, cpm.

To convert LLD to concentration, use the appropriate factors of sample volume, counting efficiency, etc. Note that the approximation  $LLD = 4.66 S_b$  can be used only for determinations where  $S_b$  is known so that  $S_o = 2^{1/2}S_b$  and there are no counting interferences. Examples of appropriate determinations are tritium, gross alpha or beta, or any single nuclide determination.

Where tracers are added to determine yield or more than one radionuclide is counted in a sample, use the general form of the above equation, for which the 95% confidence level would be:

$$LLD_{95} = 3.29S_o$$

## 4. References

1. OVERMAN, R.T. & H. CLARK. 1960. Radioisotope Techniques. McGraw Hill Book Co., New York, N.Y.
2. U.S. DEPARTMENT OF ENERGY. 1992. EML Procedures Manual, 27th ed. (rev.). HASL 300, p.4.5.29, Environmental Measurements Lab., U.S. Dep. Energy, New York, N.Y.
3. CURRIE, L.A. 1968. Limits for qualitative detection and quantitative determination—application to radiochemistry. *Anal. Chem.* 68:586.

## 7020 D. Calculation and Expression of Results

The results of radioactivity analyses usually are reported in terms of "activity" per unit volume or mass at 20°C. The recognized unit for activity is the Becquerel, Bq, equal to one disintegration per second. A commonly used unit for reporting en-

vironmental level concentrations is the picocurie (pCi) = 2.22 disintegrations per minute (dpm), or  $1 \times 10^{-12}$  Curie (Ci) or  $1 \times 10^{-3}$  nanocuries (nCi) or  $1 \times 10^{-6}$  microcuries ( $\mu$ Ci).

Specific formulas for the calculation of activity per volume or

mass are presented in the individual methods and use the general formula:

$$C = \frac{R_{net}}{e y i v d u}$$

where:

- $C$  = activity per unit volume, in units of activity/mass or volume,
- $R_{net}$  = net counting rate, cpm
- $e$  = counting efficiency, cpm/dpm,
- $y$  = chemical yield,
- $i$  = ingrowth correction factor,
- $v$  = volume or mass or portion,
- $d$  = decay factor, and
- $u$  = units correction factor.

Values for variables are method-dependent. Report results in a manner that does not imply greater or lesser precision than that obtained by the method (see Section 1030).

In reporting radiochemical data, include associated random and systematic errors, as well as minimum detectable activity. For

some intended data usage, it is necessary to report the result as calculated without regard to the sign of the absolute value, i.e., no "less than" values. The objective of data use, e.g., compliance monitoring, research, dose calculation, or trend monitoring, will dictate the data reporting format.

The following formula illustrates calculation of counting uncertainty at the 95% confidence level:

$$E = \frac{1.96 \left( \frac{R_o}{t_1} + \frac{B}{t_2} \right)^{1/2}}{e y i v d u}$$

where:

- $E$  = counting error,
- $R_o$  = gross sample counting rate, cpm,
- $t_1$  = sample count duration, min,
- $B$  = background counting rate, cpm,
- $t_2$  = background count duration, min, and
- $e, y, i, v, d,$  and  $u$  are as previously defined.